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Photochemical Reactions in Organized Monolayer Assemblies. 4. Photodimerization, Photoisomerization, and Excimer Formation with Surfactant Olefins and Dienes in Monolayer Assemblies, Crystals, and Micelles[1,2]

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Abstract: An investigation of the photoreactions of surfactant derivatives of 4-stilbazole and 1-phenyl-4-(4-pyridyl)-1,3-butadiene in various media is reported. It is found that in the solid state (with differences depending upon the negatively charged counterion) excimer fluorescence and dimerization are the dominant photoprocesses. The same processes occur in condensed monolayer assemblies; in addition, cis to trans isomerization of the surfactant stilbazole occurs but not the reverse. In contrast, for both micelles (with cetyltrimethylammonium bromide) and solutions only cis-trans isomerization and monomer fluorescence are observed; although there is some evidence of photocyclization, no dimers or excimers could be detected even at high concentrations. The differences between the solid state and monolayer behavior and that in solutions and micelles are attributed largely to the influence of packing phenomena in the former systems where all evidence points to a highly condensed structure. The prominent occurrence of excimer due to a preference for packing into dimeric sites in the condensed monolayers is consistent with the behavior observed for several other chromophores in assemblies of this sort. The contrast between the behavior of these surfactant molecules in condensed monolayers and micelles is significant since it indicates merely orienting chromophores at a hydrophilic-hydrophobic interface are insufficient to force bimolecular interactions.

Introduction

Olefins and dienes such as the stilbenes and diaryl-1,3-butadienes have been found to undergo a variety of different photoprocesses including cis-trans isomerization,[4-7] cyclization to phenanthrenes and related polycyclic aromatic hydrocarbons,[8-11] dimerization, and excimer and exciplex formation.[12-17] Although these processes have been found to occur to varying extents under different conditions in solution and in the solid state, relatively little is known about the specific influence of molecular environment on the individual photoprocesses. Much recent work has focused on the use of organized structures such as crystals,[15-18] "cracked" dimers,[19] or micelles[20-21] to elucidate details of photoprocesses and their control by molecular environment. In our own investigations we have used organized monolayer assemblies both to probe mechanistic details of photoreactions and to modify the normal solution behavior.[1,2,22,23] Recently we reported results of a preliminary investigation of a surfactant stilbene derivative prepared by N-alkylation of *trans*-4-stilbazole with the hydrophobic octadecyl group.[2] In studies of this molecule in solution, monolayer assemblies, and in crystals, it was found that its photobehavior was extremely dependent upon molecular environment. In the present paper we report results of an extended investigation of the stilbazole derivative and a similar diaryl-1,3-butadiene in a variety of media including monolayer assemblies, solids, and micelles. Results of this study emphasize the dominant role environment can play in controlling the photochemistry of these chromophores and suggest possibilities for use of the solid state and monolayer assemblies to prepare other species not obtainable in solution. An interesting aspect of this study is the finding that rather large differences exist between results obtained in micelles and in condensed monolayers. The present study emphasizes the importance of packing effects in controlling behavior in both crystals and condensed monolayers.

Experimental Section

General. Melting points were obtained on a Büchi apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. NMR spectra were obtained on a Jeolco 060H1 or Varian XL-100 spectrometer in $CDCl_3$ solution with Me_4Si as the internal standard. Absorption spectra were recorded with a Cary 17I spectrometer. Fluorescence excitation and emission spectra were recorded with a Hitachi-Perkin Elmer MPF-2A spectrophotometer. Monolayer assemblies were prepared by spreading dilute chloroform solutions of the surfactant molecules on a water surface in a trough of the type described by Kuhn and co-workers.[24] The monolayer films thus obtained were transferred to glass or quartz microscope slides by slowly passing the slides through the solution and film at a constant surface pressure (10–30 dyn/cm depending upon the mixture used). Usually mixtures of the chromophore-containing surfactant molecule and arachidic acid or tripalmitine were used. The assemblies thus obtained were examined spectroscopically on the instruments described above. Irradiations were generally carried out with 100–200 W mercury lamps using filters or a monochromator to isolate the desired emission time.

Preparation of *N*-(1-octadecyl)-4-stilbazole Salts. The salts were prepared by refluxing 1.0 g of 4-stilbazole (Eastman) with a slight excess of the alkylating agent in 30 ml of acetonitrile. The alkylating agents employed were 1-octadecyl *p*-chlorobenzenesulfonate,[25] 1-bromooctadecane (Eastman), and 1-octadecyl *p*-bromobenzenesulfonate. The reflux time was 4–6 h for the sulfonates and 21 h for the bromide. The hot reaction mixture was diluted to 100 ml with acetonitrile and allowed to cool. The solid product was collected by filtration, washed with a small amount of acetonitrile, and recrystallized from 100 ml of 2-propanol. Yields were 50–70% of theory.

***p*-Chlorobenzenesulfonate (1).** Anal. Calcd for $C_{37}H_{52}NSO_3Cl\cdot H_2O$: C, 68.97; H, 8.45; N, 2.17. Found: C, 68.83; H, 8.41; N, 2.07. UV: λ_{max} 345 nm (ϵ 23 600) in acetonitrile.

Bromide (2). Anal. Calcd for $C_{31}H_{48}NBr$: C, 72.35; H, 9.40; N, 2.72. Found: C, 71.98; H, 9.47; N, 2.43.

***p*-Bromobenzenesulfonate (3).**

Tetrafluoroborate (4). The tetrafluoroborate salt was prepared from the bromide by addition of a 10% excess of silver tetrafluoroborate (Alfa) in 2-propanol to a hot solution of the bromide salt in 2-propanol. The mixture was stirred for 15 min and filtered hot to remove the precipitated silver bromide. The product which crystallized upon cooling of the filtrate was recrystallized twice from 2-propanol. Anal. Calcd for $C_{31}H_{48}NBF_4$: C, 71.39; H, 9.28; N, 2.69. Found: C, 71.24; H, 9.33; N, 2.68. All of the *N*-(1-octadecyl)-4-stilbazole salts gave similar and good NMR spectra with the expected chemical shifts.

Preparation of 1-Octadecyl *p*-Bromobenzenesulfonate. The procedure of Sondermann[25] for the corresponding *p*-chloro compound was employed without modification using *p*-bromobenzenesulfonyl chloride (Aldrich). The product was obtained in 60% yield after two recrystallizations from methanol, mp 68.5–69.5 °C. Anal. Calcd for $C_{37}H_{52}NSO_3Br$: C, 59.03; H, 8.44; S, 6.55; O, 9.80; Br, 16.32. Found: C, 58.99; H, 8.11; Br, 16.62.

Solution Photolysis of 1 (*p*-Chlorobenzenesulfonate Salt). A nearly saturated solution of **1** (100 ml) in acetonitrile (8×10^{-3} M) was deoxygenated by bubbling with N_2 for 1 h. The solution was irradiated at a distance of 14 cm with light from a GE H100PFL44-4 reflector flood lamp filtered through 1 cm of H_2O and Corning filters CS7-54 and CS0-52 (transmitting principally 366 nm). The cis–trans photostationary state was reached within the first few hours of irradiation, and no further change was detectable after 17 h of irradiation. Prolonged irradiation of **1** in acetonitrile at spectroscopic concentrations (ca. 2×10^{-5} M) led to slow disappearance and spectral changes consistent with cyclization to the corresponding azaphenanthrene salt.

Irradiation of 9 ml of a nearly saturated solution of **1** in CH_2Cl_2 (9×10^{-2} M, deoxygenated by bubbling N_2) under the same conditions gave similar results. The cis–trans photostationary state was reached within 5 h; continued irradiation led to very slow disappearance (ca. 20% after 3 days), but the spectral changes were not consistent with dimer formation.

1 failed to dissolve to even spectroscopic concentrations in solvents such as hexane, heptadecane, and water and dissolved poorly in most other common solvents (e.g., alcohols) at room temperature, limiting the scope of the solution studies.

Solid State Photolysis of 1 and Its Photoproduct. The *p*-chlorobenzenesulfonate salt 1 (0.2 g) was spread on a 7.6-cm watch glass and irradiated at a distance of 7.6 cm with a GE H100PFL44-4 reflector flood lamp. The incident light was filtered through ca. 2 cm of water and a Corning CSO-52 filter. External cooling of the water filter was employed to maintain the temperature of the solid below 30 °C. The solid was stirred periodically and the irradiation continued until the characteristic green emission of the starting material had completely disappeared (8 h). Conversion was essentially quantitative (NMR). The dimer **5** was recrystallized from 2-propanal and air dried overnight. Anal. Calcd for $C_{74}H_{104}N_2S_2O_6Cl_2\cdot 2H_2O$: C, 68.97; H, 8.45; N, 2.17. Found: C, 68.94; H, 8.60; N, 1.98. Irradiation of the recrystallized solid dimer **5** at 254 nm (Rayonet Reactor) regenerated the green emission of **1** which could be rebleached by irradiation with the flood lamp. The *p*-bromobenzenesulfonate salt **3** dimerized completely to give the analogous dimer salt (NMR) under these conditions. The bromide (**2**) and tetrafluoroborate (**4**) salts were photostable under these conditions (NMR).

Dimerization of 4-Stilbazole in Aqueous Hydrochloric Acid. 4-Stilbazole (5.0 g) was dissolved in 500 ml of 0.114 M HCl in a 500-ml Erlenmeyer flask and irradiated with stirring for 40 h in a Rayonet Reactor (F-15D Daylight bulbs). The irradiated solution was made basic with 4.0 g of NaOH and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were washed with water, dried, and evaporated. The residue was chromatographed on 75 g of silica gel (Baker 60–200 mesh); the column was eluted with benzene, followed by mixtures of ethyl acetate (up to 20%) in benzene. Earlier fractions contained *cis*-and *trans*-4-stilbazole. Later fractions gave 2.0 g of the known syn-head-to-tail dimer **5**, which had mp 158–159.5 °C (lit.[26] mp 157–158 °C) after recrystallization from acetonitrile. The highest concentrations of ethyl acetate eluted a second dimer (**7**, 0.20 g) which had mp 196–196.5 °C after recrystallization from acetonitrile. The NMR ($CDCl_3$) of this second dimer exhibited resonances at δ 8.49 (4 H, d, $J \approx 5$ Hz, pyridyl H), 7.33 (10 H, s, phenyl H), 7.15 (4 H, d, $J \sim 5$ Hz, pyridyl H), 3.71 (4 H, unresolved m, cyclobutane H). The high resolution mass spectrum (70 eV) exhibited structurally significant peaks at *m/e* 362.1795 (3%, M^+, $C_{26}H_{22}N_2$ requires 362.1783), 182.0867 (13%, $C_{12}H_{10}N_2$ = 182.0844), 181.0821 (100%, $C_{12}H_9N_2$ = 181.0766), and 180.0711 (46%, $C_{12}H_8N_2$ = 180.0687).

Alkylation of the Dimers of 4-Stilbazole. The dimers **6** and **7** were refluxed overnight in acetonitrile with 2 equiv of 1-octadecyl *p*-chlorobenzenesulfonate. Both **8** and **9** were obtained as gel-like materials which failed to give crystalline material from either acetonitrile or 2-propanol. They were therefore isolated as gelatinous noncrystalline materials by decantation of the solvent and removal of residual solvent in vacuo overnight.

Anal. Calcd for $C_{74}H_{104}N_2S_2O_6Cl_2\cdot 2H_2O$: C, 68.97; H, 8.45; N, 2.17. Found for **8**: C, 68.83; H, 8.41; N, 2.07. Found for **9**: C, 68.87; H, 8.43; N, 2.15.

Preparation of *N*-(1-Octadecyl) Salts of *trans,trans*-1-Phenyl-4-(4-pyridyl)-1,3-butadiene (PPB). The *p*-chlorobenzenesulfonate salt **10** and the bromide salt **11** were prepared by refluxing at 1.0 g of PPB and 2.5 g of the alkylating agent (1-octadecyl *p*-chlorobenzenesulfonate or 1-bromooctadecane) in 10–15 ml of acetonitrile for 6–8 h. The products were isolated and recrystallized for 2-propanol as described for the corresponding 4-stilbazole salts. Anal. Calcd for $C_{39}H_{54}NClSO_3\cdot H_2O$: C, 69.88; H, 8.42; N, 2.09. Found for **10**: C, 69.89; H, 8.40; N, 1.97.

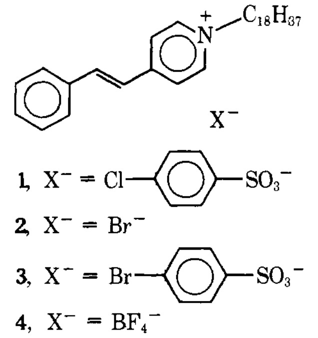
The tetrafluoroborate salt **12** was prepared from **11** and silver tetrafluoroborate in 2-propanol using the procedure described for **4**.

Anal. Calcd for $C_{33}H_{50}NBF_4$: C, 72.39: H, 9.20; N, 2.56. Found: C, 72.16; H, 9.30; N, 2.46.

Solid State Irradiation of the PPB Salts. Deoxygenated and nondegassed samples of solid **10** were irradiated as described for **1** except that the incident light was filtered through a Corning CS3-73 filter. The solid was irradiated with stirring until the characteristic orange emission of **10** had disappeared, giving a pale-yellow solid. Subsequent irradiation at 254 nm converted this material to a bright-yellow solid having a fluorescence (λ_{max} 490 nm) similar to that of solid **12**, but an excitation spectrum similar to that of **10**. Reirradiation with the filtered flood lamp reversibly regenerated the pale-yellow solid. The NMR of the photoproduct was quite complex and indicated that the product was probably a mixture of products. Attempts to separate characterizable products by recrystallization were unsuccessful.

Results

Photochemistry of *N*-(1-Octadecyl)-4-stilbazole Salts. Solution Photochemistry. Although effectively insoluble in aliphatic hydrocarbons (hexane or hexadecane) and water, salts **1–4** were moderately soluble in polar organic solvents such as



CH_2Cl_2 and acetonitrile. Solution photochemical studies with **1** gave no evidence for the presence of bimolecular interactions and indicated relatively predictable photobehavior. Acetonitrile solutions of **1** exhibited a long-wavelength absorption maximum at 345 nm (ε 23 600) and a weak structureless fluorescence with a maximum at 430 nm. Irradiation of nearly saturated solutions of **1** (8×10^{-3} M) in acetonitrile at 366 nm resulted in trans–cis isomerization with establishment of a photostationary state (pss) containing less than 30% trans-**1**. Similar results were obtained in CH_2Cl_2 solution at higher concentration (9×10^{-2} M). Slow disappearance was observed in CH_2Cl_2, but the accompanying spectral changes were inconsistent with dimer formation. Prolonged irradiation of **1** at spectroscopic concentrations in undegassed acetonitrile (ca. 2×10^{-5}) resulted in slow disappearance of **1** and spectral changes consistent with cyclization to the corresponding azaphenanthrene salt.[8]

Photochemistry in Micellar CTAB. Up to 5×10^{-4} M **1** could readily be incorporated into micellar cetyltrimethylammonium bromide (CTAB, 6.3×10^{-3} M in pH 8 phosphate buffer). Using a value of 75 for the aggregation number of CTAB[27] and assuming complete and statistical incorporation of **1** in the micellar phase, this corresponds to an average of six to seven molecules of **1** per CTAB micelle. The photochemistry of micellar **1** was quite similar to that observed in solution. Micellar **1** exhibited a long-wavelength absorption maximum at 344 nm and a weak structureless fluorescence at 428 nm. The major photoprocess upon irradiation at 366 nm was trans → cis isomerization ($\phi > 0.3$) with rapid attainment of a cis–trans pss. A subsequent disappearance process ($\phi \sim 0.01$) led to spectral changes consistent with cyclization as the major contributor.

Photochemistry in the Solid State. A distinct difference between **1** and **3** and salts **2** and **4** in the solid state was indicated by the fluorescence of the corresponding solids. Although excitation spectra were quite similar, solid samples of **1** and **3** exhibited broad, intense yellow-green emissions with a maximum at 470 nm while solid samples of **2** and **4** exhibited a weak blue fluorescence with a maximum at 430 nm (Figure 1). This difference in emission properties was nicely reflected in the solid state photochemistry of these compounds. Irradiation of **1** or **3** at long wavelengths resulted in essentially quantitative conversion of the starting material to a solid white product; in contrast, two solids **2** and **4** were recovered unchanged after irradiation under identical conditions.

The solid state photoproduct of **1** had UV absorption maxima at 257 and 223 nm (in methanol). The NMR spectrum ($CDCl_3$) indicated that the formerly vinylic protons of **1** were converted into tertiary protons with resonances at δ 5.01 and 4.75. Irradiation of the recrystallized photoproduct at 254 nm regenerated the yellow-green fluorescence of **1** which could be reversibly bleached by irradiation at 366 nm. These data are clearly consistent with a photodimer structure for the photoproduct; the absence of detectable trans–cis isomerization concomitant with photoproduct formation implies that the product must derive from the trans isomer. Thus the most reasonable assignments of the resonances at δ 5.01 and 4.75 are two cyclobutane ring protons adjacent to pyridinium and phenyl, respectively, in a *trans*-**1** + *trans*-**1** photodimer. Of the four possible dimers, **5–8**, **6** and **7** could be prepared by bisalkylation of the corresponding 4-stilbazole dimers with octadecyl *p*-chlorobenzenesulfonate. The cyclobutane ring

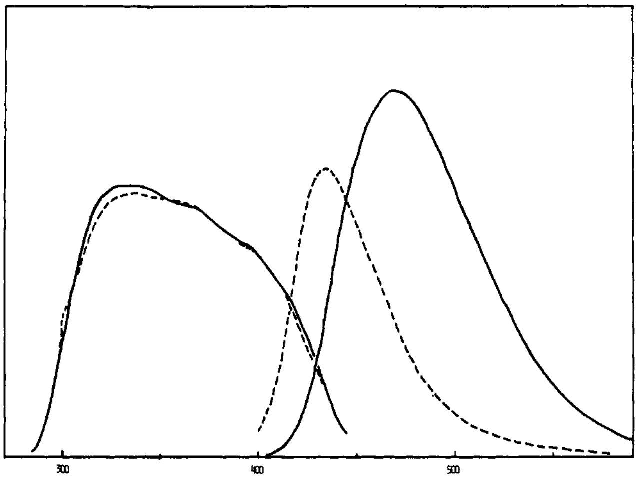
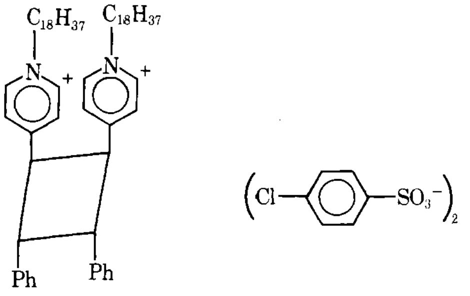


Figure 1. Solid state absorption and emission spectra: solid line shows activation and fluorescence of **1**, dashed line gives corresponding spectra for **2**.



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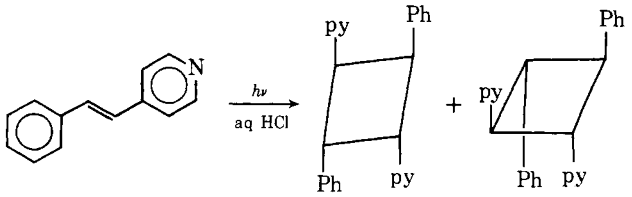
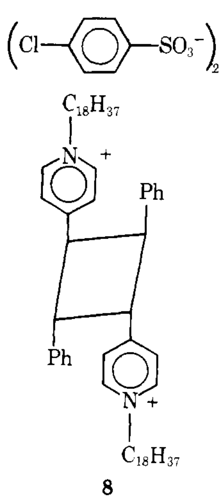


6 **7**



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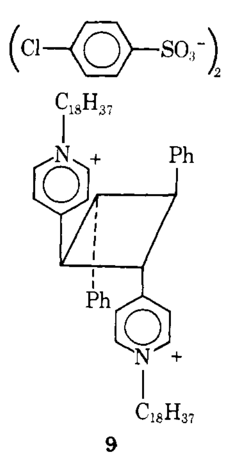

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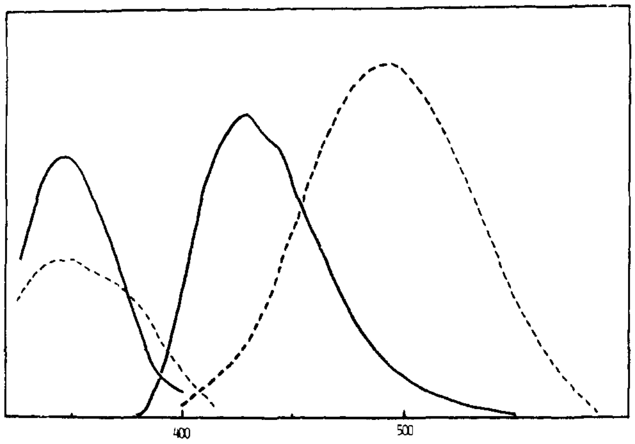


Figure 2. Absorption and emission spectra of **1** in acetonitrile solution (solid line) and in condensed monolayer assemblies (dashed line).

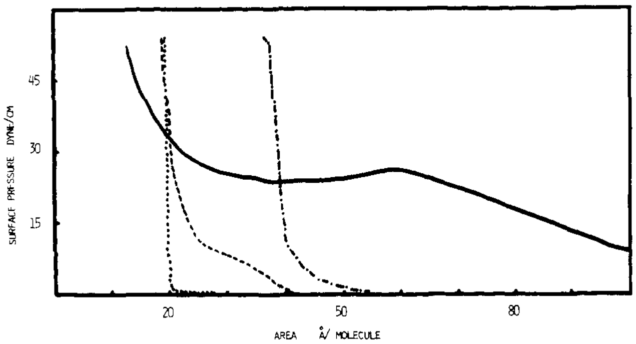


Figure 3. Surface pressure-area diagrams: (••••••) arachidic acid films; (——) films of pure **1**; (- - - - - -) calculated area of **1** in mixed **1**-arachidic acid films; (– • – • – • –) calculated area of **5** in mixed **5**-arachidic acid films.

protons appear as a 4 H resonance centered at δ 4.97 in the NMR of the trans-cis-trans dimer. In contrast, the corresponding protons[6] of the trans-trans-trans dimer[7] appear as 2 H resonances at δ 4.18 and 3.96, an upfield shift compatible with the pseudo-equatorial disposition of the four rings. Since the cyclobutyl protons of the trans-trans-trans dimer **8** should also experience a similar upfield shift, the NMR data point to **5** as the structure of the solid state photoproduct of **1**.

Photochemistry in Monolayer Assemblies. Dilute $CHCl_3$ solutions of **1–4** spread readily on a water surface in a trough of the type described by Kuhn and co-workers.[24] Monolayer films of the pure compounds or in mixtures with arachidic acid or tripalmitine (TP) were stable at surface pressures of 15–20 dyn/cm, and monolayer assemblies incorporating **1–3** could be readily constructed on quartz or glass slides by the usual techniques. Absorption spectra of various assemblies containing **1** are similar (λ_{max} 345 nm) to those in acetonitrile solution (Figure 2), but are somewhat broader on the long-wavelength side. Studies with polarized light indicated that the transition moment of the long-wavelength band of **1** in the assemblies lies principally in the layer plane. Since this transition is probably in the molecular plane, this suggests that the long axis of the chromophore of **1** is largely oriented parallel to the layer plane. Surface pressure-area diagrams for **1** in mixtures with arachidic acid yielded areas in the range of 24–40 Å^2/chromophore for pressures in the range of 15–20 dyn/cm (Figure 3), significantly smaller than the area of ca. 85 Å^2 calculated for a planar *trans*-4-stilbazole molecule on the basis of models.

Irradiation of assemblies containing *trans*-**1** results in two detectable photoprocesses. The first is intense yellow-green fluorescence ($\phi \geq 0.1$) with a maximum at about 490 nm (Figure 2), considerably red shifted from the emission in solution but quite similar to that of **1** in the solid state (Figure 2). The second process is bleaching of the long-wavelength absorption band upon irradiation at 366 nm with a concomitant increase in adsorption at 265 nm and loss of the 490-nm emission. After bleaching has ceased, a residual blue fluorescence similar to that of the monomer in solution is observed. The rate and extent of this process is strongly "concentration" dependent, and the interposition of "spacer layers" of arachidic acid between layers containing **1** lowers both the rate and extent of the reaction (Figure 4). The quantum yield for this process is quite high ($\phi \geq 0.1$) at the higher concentrations of **1**. These data, combined with the observation that assemblies incorporating the solid state dimer of **1** exhibited an absorption similar to that of the photoproduct in the assemblies, indicate that a photodimerization to give products of the cyclobutane type is responsible for the second process.

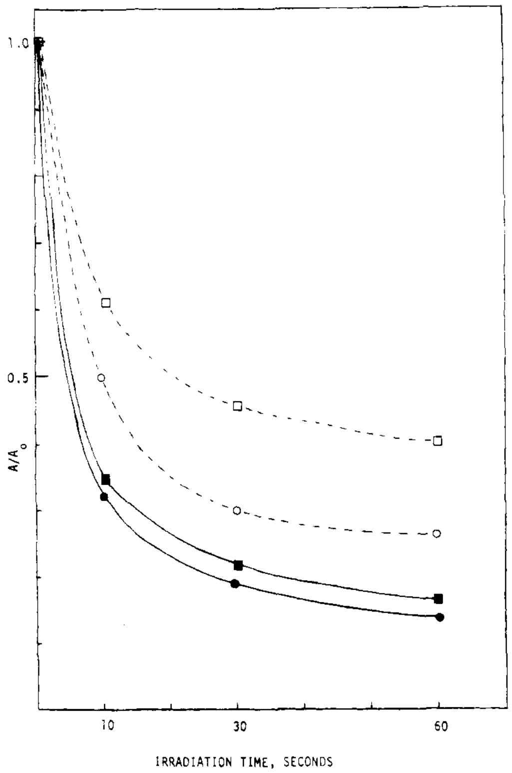


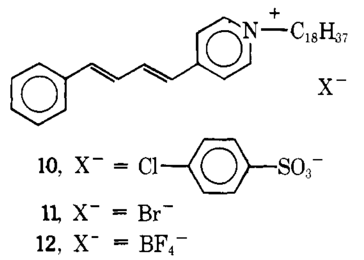
Figure 4. Plot of A/A_0 vs irradiation time for monolayer assemblies of **1** with tripalmitine and arachidic acid: (—●—) six adjacent layers of **1**:TP in a 1:4 ratio; (—■—) six adjacent layers of **1**:TP, 1:8; (—○—) six layers of **1**:TP, 1:4 alternating with layers of pure TP; (—□—) six layers of **1**:TP, 1:8 alternating with layers of pure TP.

Although there are clear parallels between the solid state and monolayer assembly results for **1**, irradiation of reacted assemblies of **1** or assemblies prepared from the solid state dimer of **1** at 254 nm does not lead to detectable regeneration of the 490-nm emission band. Moreover, although salts **2** and **4** exhibit no photoreactivity in the solid state, monolayer assemblies constructed from **2** and **4** show essentially identical properties and photochemical behavior with those prepared from **1** and **3**.

Monolayer assemblies could also be prepared (in the dark) from chloroform solutions of **1** which had been irradiated at 366 nm until a photostationary state had been attained. Irradiation of these assemblies yielded rather interesting results. Freshly prepared assemblies showed fluorescence similar to that observed from assemblies prepared from *trans*-**1**; however, the intensity of the fluorescence was much weaker than those prepared from isomerically pure *trans*-**1**. On irradiation, the fluorescence could be observed to increase significantly and then subsequently decrease. The fluorescence behavior was coupled with changes in the absorption spectrum: the long wavelength transition at 350 nm first increased slightly but with subsequent irradiation it showed bleaching similar to that observed on irradiation of assemblies containing isomerically pure *trans*-**1**.

Photochemistry of *N*-(1-Octadecyl) Salts of *trans,trans*-1-Phenyl-4-(4-pyridyl)-1,3-butadiene (PPB). The photoreactions of the diaryl butadiene analogues of the surfactant stilbazoles have been investigated in relatively preliminary fashion. Although their behavior appears to be considerably more complicated than that of the stilbazoles, there are several significant similarities that indicate results obtained with the stilbazoles salts are probably rather general.

Monolayer assemblies constructed from arachidic acid and any of the three salts prepared (**10**, **11**, or **12**) all show similar behavior. The fluorescence is considerably red shifted from that obtained in solution; a red-orange fluorescence (λ_{max} ca. 550 nm) is obtained from assemblies constructed from pure **10** or from 3:10 mixtures with arachidic acid. A surface pressure-area determination with films of pure **10** gives an area/molecule in the film of ca. 75 Å^2 at a surface pressure of 20 dyn/cm. The films are transferable at this point but not very stable. Better films and assemblies could be prepared by using arachidic acid-**10** mixtures. With mixtures of **10**-arachidic acid in the ratios 1:2, 1:5, or 1:10, films were obtained that formed good assemblies and were stable up to ca. 50 dyn/cm. In all three of these mixtures the area/molecule of **10** calculated from difference pressure-area diagram was ca. 22 Å^2 at surface pressures ca. 30 dyn/cm (Figure 5). Thus the pressure-area diagram behavior of films of the PPB salts is nearly identical with that observed for films of the stilbazole salts. Polarization spectra obtained for assemblies formed from **10**-arachidic acid mixtures indicate that the transition moment of the long-wavelength absorption lies randomly in the plane of the assemblies.



Irradiation of assemblies containing either pure **10** or **10**-arachidic acid mixtures leads to rapid disappearance of the long-wavelength transition in a manner reminiscent of the behavior of the surfactant stilbazole salts. The product has a blue-green fluorescence and appears to be photostable; no reversion to the initial material could be induced by irradiation with short-wavelength light. In contrast to the results obtained with assemblies containing the stilbazole salts, there appeared to be little, if any, effect produced on the rate of the photobleaching by the interposition of "spacer layers" of arachidic acid between layers containing the PPB salts. Thus in contrast to the stilbazole salts where both inter- and intralayer dimerization apparently occur, photodimerization in assemblies containing **10** is exclusively an intra-layer process. The rate and quantum efficiency of disappearance of the PPB salt in the assemblies is approximately the same as that observed for layers containing comparable "concentrations" of the stilbazole salts.

The solid state behavior of **10** is also similar to that of the *p*-chlorobenzenesulfonate salt of *N*-(1-octadecyl)-4-stilbazole (**1**). The crystals of **10** exhibit a fluorescence ($\lambda_{max} \simeq 545$ nm) strongly red shifted from that observed for solutions of **1**. In contrast, crystals of the fluoroborate salt (**12**) fluoresce with λ_{max} 490, close to the solution fluorescence. While **12** is photostable in the solid state, the dark yellow crystals of **10** rapidly undergo a photoreaction under irradiation to yield a pale-yellow product (**13**). The NMR of the photoproduct (**13**) was quite complex and even repeated recrystallization failed to yield an identifiable single product. Irradiation of the crude photoproduct **13** with short wavelength (254 nm) light generates a darker yellow material having a fluorescence λ_{max} at 495–500 nm. Although the major fluorescence was shifted from that of unirradiated **10**, the excitation spectrum of this solid photoproduct was identical with that obtained for crystals of **10**. This product upon irradiation with the photoflood lamp used to irradiate **10** formed pale-yellow crystals which appeared identical with **13**. The NMR spectrum of **13** suggests that the photoproduct is a mixture, perhaps containing two or more cyclobutane dimers. Although previous reports suggest that dimers formed from other diaryl butadienes do not interconvert,[17,28] it is reasonable to expect that Cope rearrangements could convert a single initial product into a mixture of interconverting isomeric products.

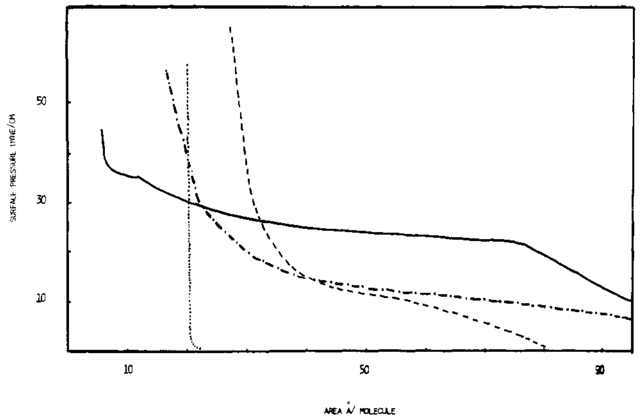
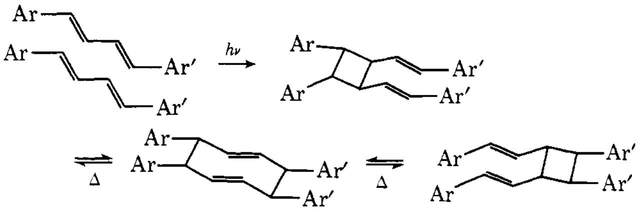


Figure 5. Surface pressure-area diagrams for PPB-arachidic acid films: (• • • • • •) arachidic acid; (——) pure PPB; (- - -) arachidic acid:PPB, 2:1; (- • - - •) calculated area of PPB in the mixed film.

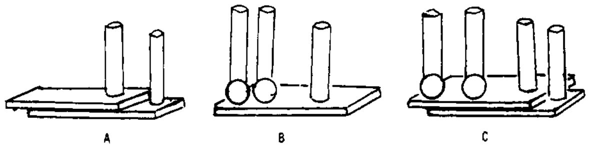


Discussion

Perhaps the most striking aspect of the results obtained in this investigation is the contrast in behavior of the surfactant olefin and diene between, on the one hand, solution and micelles (where similar behavior is observed) and, on the other, the solid and the monolayer assemblies. Both the solid state and monolayer photobehavior are characterized by two processes not observed in the other media: dimer formation and red-shifted fluorescence. It is reasonable that the red-shifted fluorescence originates from an excimer state. Although there are no data concerning the behavior in either the solid state or the assemblies that permit a distinction between a discrete excimer state or a delocalized aggregate or excitonic state, the observation that the spectra obtained are rather intense and similar to those which have been obtained previously for excimers formed from similar molecules umder other conditions[15,17,28] suggests that these most likely are also excimers. It is also reasonable but not established that the excimer is an intermediate on the path to dimer formation in the solid and assemblies.

Considering first the behavior observed on irradiation of crystals of **1**, **3**, and **10**, it is not too surprising that excimer fluorescence and photodimerization occur since other substituted stilbenes and diaryl-1,3-butadienes have been found to show similar behavior in the solid state.[15,17,28] However, the specific product formed on photodimerization of crystals of **1** and **3** is rather surprising since although the substituted stilbenes and diaryl-1,3-butadienes studied previously form syn-head-to-head dimers,[15,17,18] the dimerization of quaternary stilbazole salts and other quaternary salts of N-heteroaromatics in the solid state has been reported to yield almost exclusively head-to-tail structures.[14,29] Although crystal structures are not available for most of the N-heteroaromatic quaternary salts, it appears reasonable that in the crystal a head-to-tail alignment is preferred in order to minimize steric and like-charge repulsions. For **1** and **3** the apparent favoring of a structure in which a syn-head-to-head alignment occurs suggests that preferential association of hydrophilic zones and of hydrophobic zones occurs. Since attractive forces between nonpolar groups are rather weak[30] and since a parallel arrangement of the polar groups in **1**, **3**, and **10** undoubtedly involves considerable like-charge repulsion, the preferential association probably arises from a crystal packing phenomenon in which molecular shape such as the regular structure of the polymethylene hydrocarbon chain plays a major role. Ordered hydrocarbons typically have an interchain spacing of ca. 4.2 Å,[31] and a spacing of this order has been shown by Schmidt et al.[32] to be near the limit within which properly aligned monomers in a crystal can dimerize. It would appear reasonable that a crystal structure controlled by packing phenomena such as those described above should be extremely dependent on the counterion incorporated into the lattice. Thus the failure of **2**, **4**, or **12** to yield photodimer or excimer fluorescence should not be surprising. It is frequently observed that phospholipids and similar substances undergo phase transitions below their melting points in which the hydrocarbon chains change from an ordered to more liquid-like state with a corresponding increase in the interchain separation from 4.2 to 4.6 Å.[31] Interestingly, it is found that heating of crystalline **1** results in reversible loss of the "excimer" emission at temperatures considerably below the melting point. While this could simply reflect the generation of traps which cause deactivation of the excited state, it could also be due to "melting" of the crystalline hydrocarbon regions with a corresponding "release" of the chromophores from close proximity to one another.

The results obtained in the monolayer assemblies seem also to indicate the importance of packing phenomena in controlling the observed photobehavior. The area/molecule obtained in the surface pressure range (25–30 dyn/cm) where the most stable films are formed and the assemblies are constructed in ca. 20–24 Å^2 for **1–4** and **10** in mixed layers with arachidic acid. These values are very close to the value of 20 Å^2 which is obtained for arachidic acid itself in pure layers.[24,33] This value is typical for hydrocarbon chains in condensed monolayers and about the same as the cross-sectional area of hydrocarbon chains as determined by x-ray analysis in crystals.[34] As described above, the polarization spectra indicate that the chromophores in monolayer-bound **1–4** and **10–12** lie in the layer plane; molecular models indicate the planar stilbazole molecule should occupy an area of ca. 85 Å^2 and the diaryl-1,3-butadiene chromophore of **10–12** should be somewhat larger. Thus it is clear that there is an imbalance between the "cross-sectional" areas of the hydrophobic and hydrophilic portions of these surfactant molecules. The fact that the cross-sectional area measured for **1–4** and **10–12** in the mixed layers corresponds to the area of the hydrophobic hydrocarbon group and not to the chromophore indicates that packing of the hydrocarbon chains into a "crystalline" lattice probably occurs with concomitant pairing up of the chromophores or packing of arachidic units "over" the chromophore or a combination of the two as illustrated in structures A–C, respectively.[35] That photodimerization can occur without demanding major changes in the layer structure is suggested by the finding that dimer **5** forms good films in mixtures with arachidic acid in which the extrapolated area/molecule of **5** is ca. 40 Å^2 or a little less than twice the monomer area at surface pressures in the range 20–30 dyn/cm. The observation that the long-wavelength emission and dimer formation in the assemblies persists (though with reduced efficiencies) even at high mixing ratios (greater than 1:20 of **1**:arachidic acid) must reflect the preference of sites such as A or C in the assemblies. Nevertheless the presence of monomeric sites such as B is also indicated by the failure of dimerization to go to completion and the presence of some residual monomer emission after the photobleaching has ceased.



The similarity in the results for **1–4** in the assemblies indicates that the nature of the counterion is of little consequence and serves to emphasize that it is the preferential packing of the stilbazole part of the molecule into these sites which determines the ultimate photobehavior of the assembly.[36]

The contrast between the results in micelles and monolayer assemblies is quite significant. In the micelles only photoisomerization of **1** similar to that occurring in solution (and perhaps subsequent cyclization) is observed. No excimer emission or photodimerization could be detected. The experiments with micelles involved about six to seven molecules of **1** in micelles of CTAB which contain on the average 75 molecules total.[27] This corresponds to mixing ratios of 1:10–1:12 in the monolayer assemblies, ratios at which significant excimer fluorescence and dimer formation occurs. The absence of excimers in the micelles then indicates that merely orienting the stilbazole chromophore at a hydrophilic–hydrophobic interface at low effective surface pressure is insufficient to bring about the needed bimolecular interactions. One reason for the differences between micelles and monolayers in the present case may be the lack of order in the former state. The hydrocarbon chains in many micelles have been found to be generally disordered such that the hydrophobic core is effectively liquid hydrocarbon.[31] Under these conditions there should be no selective packing of the chromophores together such as has been suggested above for the solid and high surface pressure monolayers. If the hydrocarbon chains are coiled instead of packed upright (as in condensed monolayers), the presence of the hydrocarbon chain on the chromophore could inhibit approach of two chromophores within ca. 4.2 Å of one another with appropriate geometry for excimer formation or cyclodimerization. This likely occurs for solutions of **1** and the other surfactant olefins and dienes. While excimers are not generally found from stilbenes and diaryl-1,3-butadienes in solution,[12] the stilbenes do photodimerize in solution.[37–39] In contrast, no dimers were formed from **1–4** or **10** even at the limits of solubility in acetonitrile or chloroform. Thus, whether the excimer states of **1**, **3**, and **10** are repulsive insofar as the chromophore is concerned remains uncertain. The results in the micelles would suggest this to be the case; as mentioned above, the solution behavior could simply reflect steric factors introduced by the hydrocarbon chains. In any event it appears that in the assemblies and the solid state, packing of the hydrocarbon chains physically constrains the two molecules to a dimer geometry, thus effectively offsetting any intermolecular repulsion and forcing the molecule into the bound region of the excimer potential.

The observation that excimers not observable in solution can be generated in the condensed assemblies is consistent with the behavior of other chromophores incorporated variously into hydrophilic and hydrophobic portions of monolayer assemblies. For example it has been found that surfactant porphyrins incorporated into hydrophilic regions selectively pack into dimeric sites;[40,41] prominent excimer fluorescence is also observed from pyrene chromophores incorporated in the hydrophobic region of assemblies even at very low dilution.[42] Thus it might be anticipated that the monolayer assembling technique will prove useful for generating other excimers not obtainable in solution.

In an earlier study, we demonstrated that the monolayer assembly structure is sufficiently rigid to inhibit trans to cis isomerization of surfactant thioindigo dyes incorporated into layers.[22] In this system the cis to trans conversion, which is accompanied by a contraction in surface area, still occurs readily although at somewhat lower efficiencies than in solution.[22] The failure to cleave the photodimer of **1** with short wavelength light and the occurrence of photoisomerization only in the cis to trans direction for **1** in the assemblies appear to be other examples of the rigidity effect. That the former phenomenon may be due to the layer structure is indicated by the finding that the solid photoproduct from assemblies containing **1**, recovered by chloroform extraction, undergoes conversion to a product having what appears to be the normal excimer fluorescence of **1** upon irradiation with 254 nm light. The occurrence of photoisomerization with **1** only in the cis to trans direction is consistent with the thioindigo results since for the structurally similar stilbenes the molecular volume of the cis isomer is larger than that of trans.[6,43]

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(36) The counterion present in the assemblies was not specifically determined; it is possible that exchange of the counterion occurs in the subphase during film formation such that **1–4** in the films are identical.

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